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(56) Documents Cited  
**EP 0814067 A1 EP 0618344 A2**  
**EP 0611081 A2 US 5447198 A**  
**US 4933031 A US 4877452 A**  
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**JP11001362**

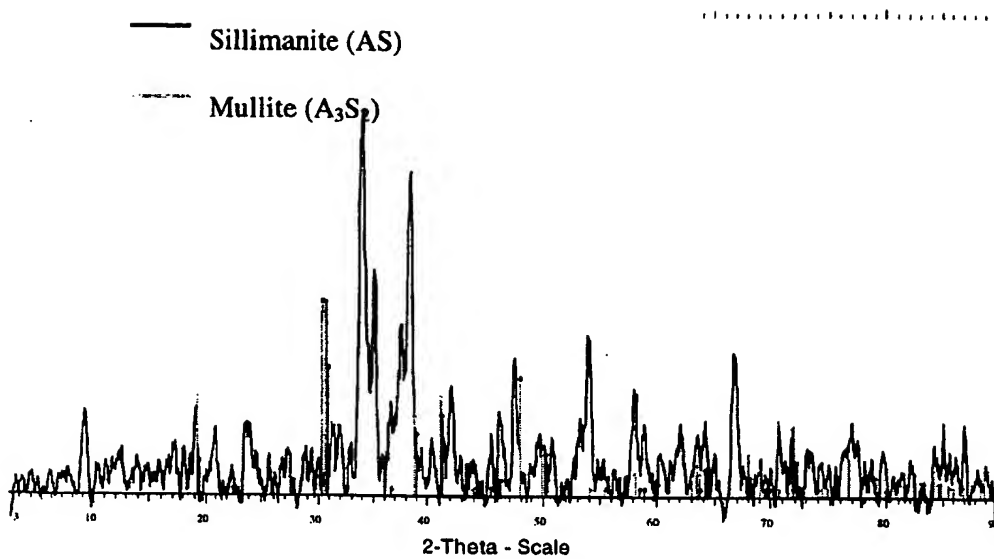
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(54) Abstract Title  
**Impermeable oil well cement**

(57) An oil, gas or water well cementing composition comprises a blend of Portland cement and pozzolanic materials (blast furnace slags, fly ash, etc.) Such that the chemical composition, expressed in oxides, has a CaO/SiO<sub>2</sub> molar ratio below 1.7. A preferred composition is a mixture of Portland cement and blast furnace slags with more than 60% of slags. The Blaine fineness of this material can be between 2,500 and 12,000 cm<sup>2</sup>/g and preferentially between 3,000 and 5,000 cm<sup>2</sup>/g. Hollow particulate material such as cenospheres, glass microspheres or ceramic spheres, may be added to the composition. The spheres remain in tact when combined with the cementitious materials, and do not cause the final composition to become porous.

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Figure 1



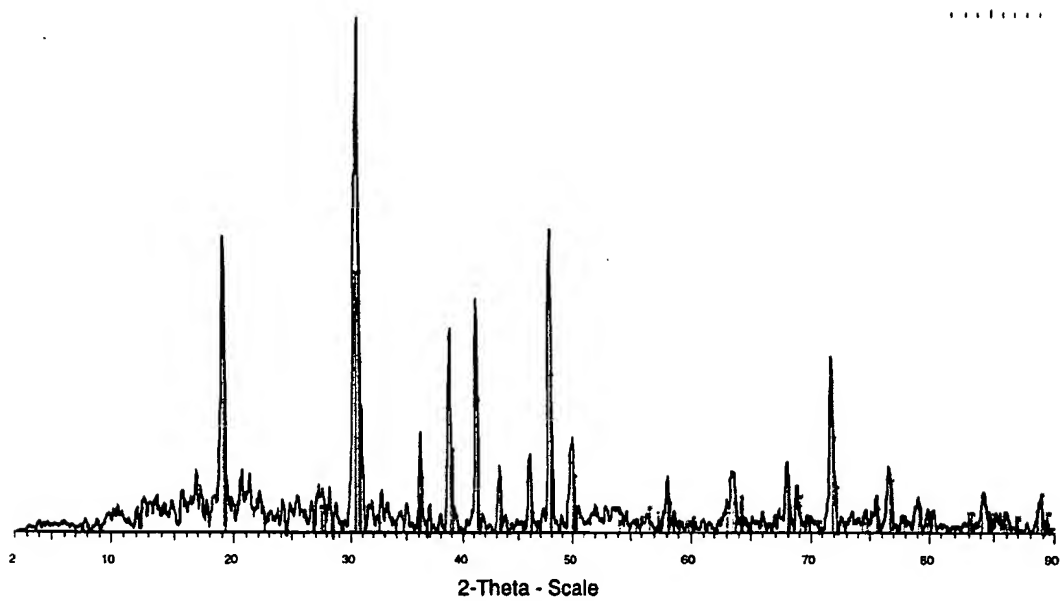


Figure 2

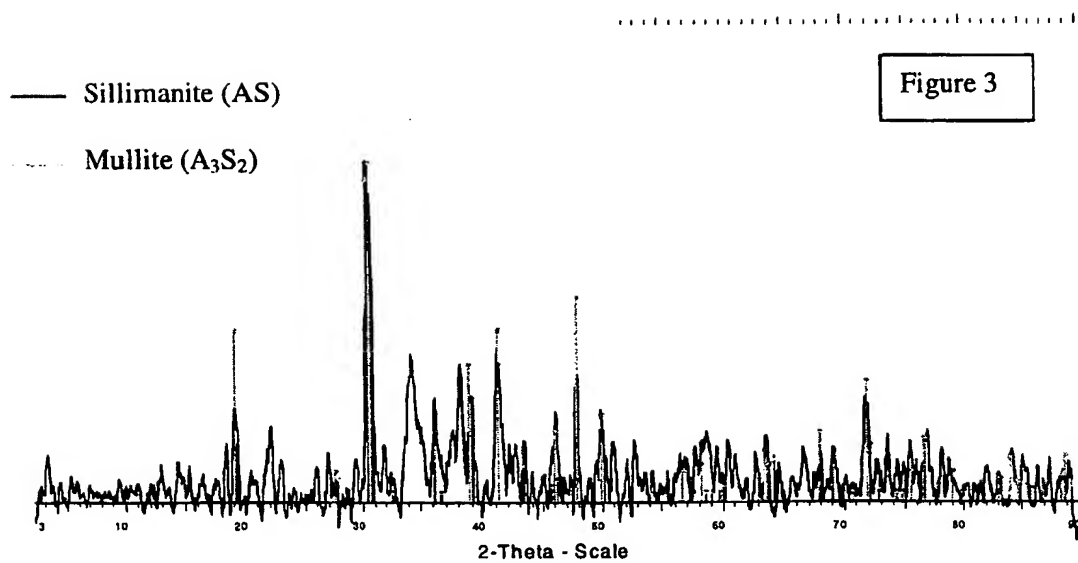


Figure 3

## OIL WELL SLAG CEMENTS

The present invention relates to oil well cements containing a relatively high amount of slag. In particular, the invention relates to cementing compositions including such cements and hollow particles.

Oil well cements are often manufactured to comply with the American Petroleum Institute specification 10 which specifies chemical and physical parameters to which the cement must adhere. These parameters include compositional requirements and physical limits such as fineness. API Class G oil well cement is defined as a basic cement in which no additives are interground or blended during manufacture. As manufactured it is considered appropriate for use from surface to 8000 ft (2440m) depth, or can be used with chemical admixtures to cover a wider range of temperatures and depths.

The basic chemistry of oil well cements is similar to that of construction cements but hydration generally occurs at a slower rate. Standard conditions for hydration reactions in actual wells are non existent (conditions vary from well to well and even within a single well), therefore the behaviour of oil well cement products depend on the particular conditions encountered which affect the reaction.

Oil well cements are often used with the addition of admixtures to obtain the required slurry properties, depending on the well conditions i.e. temperature and pressure. These admixtures are used in combination and include, for example, retarders, antifoam agents, dispersants and fluid loss controllers.

All oil well cements which comply with the API specification have a similar  $\text{CaO/SiO}_2$  molar ratio close to 3. They differ from each other mainly by their fineness and the amounts of  $\text{C}_3\text{A}$  and  $\text{C}_3\text{S}$  phases ( $\text{C}=\text{CaO}$ ,  $\text{A}=\text{Al}_2\text{O}_3$ ,  $\text{S}=\text{SiO}_2$ ,  $\text{H}=\text{H}_2\text{O}$ ). The amount of  $\text{C}_3\text{A}$  is critical for the chemical durability to sulphates and has also a significant impact on the rheological properties of cement slurries. Most oilwell cements are commercially

available as MSR (moderate sulphate resistant,  $3\% < C_3A < 8\%$ ) or HSR (high sulphate resistant,  $C_3A < 3\%$ ).

Due to their similar chemistry, oil well cements generate the same hydrates. When the curing temperature is above 230°F (110°C), it has been proposed to add up to 35% of silica to the cement to avoid the formation of the alpha dicalcium silicate phase ( $\alpha$ -C<sub>2</sub>SH) which is detrimental for the mechanical properties and the permeability of the set cement (often known as "strength regression").

The present invention provides an oil well cementing composition comprising a blend of Portland cement and pozzolanic materials (blast furnace slags, fly ash, etc.) such that the chemical composition (expressed in oxides) has a CaO/SiO<sub>2</sub> molar ratio below 1.7.

A preferred composition is a mixture Portland cement and blast furnace slags with more than 60% of slags. The Blaine fineness of this material can be between 2,500 and 12,000 cm<sup>2</sup>/g and preferentially between 3,000 and 5,000 cm<sup>2</sup>/g.

Oil well cementing compositions according to the present invention relates have a chemical composition significantly different from conventional oil well cement, and provide the following benefits :

- below 230°F (110°C), the amount of portlandite (Ca(OH)<sub>2</sub>) that is formed during hydration is significantly reduced and the amount of C-S-H gel increased. This results in a denser matrix which is much less permeable and shows better resistance to brines.
- Above 230°F (110°C), the alpha dicalcium silicate phase which is detrimental for the mechanical properties and the permeability, is not formed, and by consequence the addition of silica is not needed (thus avoiding the need to blend cement and silica on-site and avoiding the need to handle fine silica materials).
- When combined with cenospheres, the material does not induce the hydration of these cenospheres due to the lack of portlandite. As a consequence, the

porosity of the cement does not increase during hydration, so the permeability of the resulting set cement is lower and the chemical durability better.

- The cement material can also be used in a cementing composition having an engineered particle size distribution designs as fine particles for slurries with density below 10 ppg (pound per gallon) or as medium particles for slurries above 10 ppg.
- The amount of  $C_3A$  is typically very low (below 3%) in this material which makes it an inherently high sulphate resistant material.

Fly ash that is formed during the process of coal combustion in typical steam power plant generation contains a certain amount of fine spherical particles known as "cenospheres" (also called glass beads, hollow ceramic spheres or microspheres). Due to their unique combination of spherical shape, controlled sizing (after processing), relatively high strength in uniform compression, good thermal and acoustical insulating and dielectric properties, many high value applications can be made with these materials. Cenospheres have various applications which include lightweight mineral fillers in oil well cement slurries.

Cenospheres are hollow alumino-silicate vitreous spheres filled with air and/or gases. Their shell thickness is about 5% of the diameter. Alumino-silicate glass predominates with negligible crystalline matter. However, a few spheres have significant crystal growth of mullite ( $Al_6Si_2O_{13}$ ).

Cenospheres are relatively, chemically inert and offer a good resistance to solvent and acids, but in presence of calcium and at high pH (>13), silicoaluminates react with calcium to produce a cementitious material composed of calcium silicate hydrate (called "C-S-H gel") containing aluminium ions.

When cenospheres are combined with Portland cement to provide light weight slurries, these chemical criteria are met. As the Portland cement starts to set, there is a significant increase of pH due to the release of alkalis into the liquid phase, and calcium hydroxide is

always available. At that point, cenospheres start to hydrate. Due to the small thickness of the shell, the void inside the particle becomes rapidly part of the porosity of the set cement matrix. However, the cementing composition of the present invention avoids this problem since there is relatively little calcium hydroxide present with which the cenospheres can react. Because the reactivity of the cenospheres can be controlled, it is possible to produce very low density slurries using a combination of cenospheres and foam with a reduced risk of excessive permeability being produced in the resulting cement.

This and other advantages of the present invention will be demonstrated by the following examples and with reference to the accompanying drawings, in which:

Figure 1 shows X-ray diffraction spectrum of a set Portland cement with cenospheres;

Figure 2 shows X-ray diffraction spectrum of cenospheres; and

Figure 3 shows X-ray diffraction spectrum of a cement composition according to the invention with cenospheres.

#### Experiment I

This experiment demonstrates the chemical reactivity of cenospheres with conventional Portland cement :

A cement slurry was prepared by mixing :

- a blend of Portland cement Class G, and cenospheres (specific gravity of 0.75, average particle size 130 microns) present in an amount of 35% by weight of cement;
- a mixing fluid composed of 10.1 gallons per sack (gps) of cement of water, 0.04 gps of liquid antifoam and 0.4 % by weight of blend (BWOB) of an antisetling agent.

The mixed slurry has a specific gravity of 1.32 (11 ppg).

This cement slurry is then cured in a curing chamber under 3000 psi at 302°F (150°C) for 5 weeks. After, cooling, the set cement is dried with acetone and ethyl ether and then analysed :



#### 1) X ray diffraction characterization

The X-ray diffraction spectrum of the sample is shown in Figure 1 and can be compared with that of cenospheres as shown in Figure 2. No peaks specific of the mullite phase (arising only from cenospheres) can be observed in this sample as can be seen in the spectrum (Figure 1) indicating that the cenospheres have reacted during the curing process and have broken down.

#### 2) Scanning electron microscopy (SEM)

SEM analysis of the sample shows that the integrity of the shell of the cenospheres is not maintained. Most of the spheres are opened.

### Experiment II

The chemical composition of the cementitious material according to the invention (20% Portland cement/80% slags in this example), there is no calcium hydroxide available to promote the reactivity of the silicoaluminates in the cenospheres. This can be shown by doing the same experiment as in I above but replacing the Portland Class G cement by the cementitious material according to the invention, exactly in the same amount :

#### 1) X ray diffraction characterization

The peaks specific of the mullite phase (indicating the presence of complete cenospheres) can be easily observed in this sample as can be seen in the spectrum (Figure 3) when compared to the spectrum of the cenospheres (Figure 2).

#### 2) Scanning electron microscopy

By SEM one can observe that the integrity of the shell of the hollow spheres is maintained.

Contrary to Portland cement, when combined with cenospheres, the cementitious material according to the invention does not induce any chemical modification of these cenospheres. As a consequence, the voids which compose the core of the cenospheres are

not part of the porosity of the set material, that decreases significantly the permeability and increase the chemical durability when compared to normal Portland cement.

Cenospheres are known to have a higher chemical resistance to brines but also to acids compared to cementitious hydrates. By avoiding their hydration when combined with a cementitious material, the chemical durability of the set cement matrix is improved.

### Experiment III

The following slurries are prepared :

- a. Class G cement was mixed with fresh water, 0.03 gps of antifoam, and 0.04 gps of dispersant so that the density of the slurry is 16 ppg (cement slurry porosity of 59%);
- b. Class G cement is blended with cenospheres (specific gravity of 0.75, average particle size 130 microns) respectively in 40%/60% volume ratio. This blend is then mixed with fresh water, 0.03 gps of antifoam, and 0.4% by weight of blend (BWOB) of anti-settling agent so that the density of the slurry is 11.4 ppg (cement slurry porosity of 50%).

These two cement slurries are cured under 3000 psi at 185°F (85°C) for 72 hours.

The cement cubes are weighted, then immersed into a 12% HCl solution. After 24 hours, the weight loss of the cubes made from the blend Class G/cenospheres was 31% greater than the neat Class G.

This experiment is repeated with the same slurry designs but with a cementitious material composed of 20% Portland cement and 80% slag (cement X) :

- c. Cement X is mixed with fresh water, 0.03 gps of antifoam, and 0.05 gps of dispersant so that the density of the slurry is 15.2 ppg (porosity 59%).
- d. Cement X is blended with cenospheres (specific gravity 0.75, average particle size 130 microns) respectively in a 40%/60% volume ratio. This blend is then

mixed with fresh water, 0.03 gps of antifoam, and 0.4% BWOB of anti-settling agent so that the density of the slurry is 11 ppg (cement slurry porosity of 50%).

These two cement slurries are cured under 3000 psi at 185°F (85°C) for 72 hours.

The cubes are weighted, then immersed into a 12% HCl solution. After 24 hours, the weight loss of the cubes made from the Cement X/cenospheres is 23% less than the neat Cement X.

This experiment demonstrates that maintaining the integrity of cenospheres can improve significantly the chemical durability of the set cement.

By using the appropriate cementitious material, one can control the chemical reactivity of cenospheres. Depending on the final properties of the set cement which are required, this reactivity can be enhanced or prevented (chemical resistance).

Preventing the chemical reactivity of cenospheres has a tremendous impact on the permeability. Foaming cement slurries with nitrogen to obtain light weight cement is commonly used. However, it is also well known that foaming is detrimental for the final permeability of the set material. Therefore, a foamed cement slurry containing cenospheres and Portland cement will give a final material with a high permeability (> 0.1 mDarcy).

The following example will show how the permeability can be significantly reduced when in such systems Portland cement is replaced by a cementitious material as defined by the invention.

#### Experiment IV

The following cement slurries are prepared :

- a) Cement X is blended with cenospheres (specific gravity of 0.75, average particle size 130 microns) respectively in a 40%/60% volume ratio. This blend is then mixed with fresh water, and 0.08 gps of surfactants are added and the slurry is mixed in a closed warring blender so that the foam quality is 30 % (that is the volume of gas represents 30% of the total volume of cement slurry). The final density of the slurry is 7.6 ppg.
- b) Class G cement is blended with cenospheres (specific gravity of 0.75, average particle size 130 microns) respectively in a 40%/60% volume ratio. This blend is then mixed with fresh water, and 0.08 gps of surfactants are added and the slurry is mixed in a closed warring blender so that the foam quality is 30 %. The final density of the slurry is 7.9 ppg.

These two cement slurries are cured at 185°F (85°C) in a close cell (to avoid gas expansion) for 48 hours. The water permeability of the set materials is then measured :

- Formulation with Class G cement: 10 mDarcy
- Formulation with Cement X : < 0.1 mDarcy

There is at least 2 orders of magnitude in the permeability which is a significant improvement. The cementitious material related to the invention is therefore particularly efficient to foam cement slurries containing cenospheres, allowing to reach very low densities but still keeping an acceptable permeability (< 0.1 mDarcy).

Cement compositions according to the invention can form part of an engineered particle size distribution system such as that described in EP 621247. Engineered particle size distribution is a concept that optimises the Packing Volume Fraction (PVF) of a blend of solid particles which allows the preparation of slurries with a high content of solid (up to 62% of the total volume of slurry) with a low rheology. This optimised PVF is achieved by choosing an appropriate combination of particles in term of particle size and ratio. As long as these size criteria are met, the different particles may have any specific gravity, allowing the preparation of slurries from 6 ppg to 24 ppg. The cementitious material

according to the invention can be used instead of Portland cement in such slurries and preferentially when cenospheres are one of the other particles. This will reduce the total porosity of the set cement as it does not induce the hydration of the cenospheres.

#### Experiment V

A blend of a cementitious material (20% Portland/80% slags, the mixture having an average particle size of 12 microns) with Cenospheres having a particle size distribution (average particle size of 130 microns) such that the blend has a PVF around 0.8 and a specific gravity of 1.17, is prepared. A mixed fluid containing 6.71 gpsb (gallon per 100 pounds of blend) of water, 0.07 gpsb of a liquid antifoam, 0.6 gpsb of a fluid loss control agent, 0.03 gpsb of retarder and 0.01 gpsb of a dispersant is prepared. When the blend is mixed with the mixed fluid, the cement slurry density is 1.1 (9.2 ppg).

The system properties are as follows:

Slurry Density	1.10 (9.2 ppg)
Slurry Porosity	42%
Plastic Viscosity (mPa.s)	111
Yield Stress (Pa)	1.4
Thickening time	3 hours
Compressive Strength at 24 hours	13.8 MPa (2000 psi)

The rheological values (Bingham model) are obtained after conditioning for 20 minutes the cement slurry at 130°F (54°C).

The final compressive strength is measured after a cure of 24 hours at 158°F (70°C).

The water permeability measurement is below the detection limit of the test equipment used (5 micro Darcy).

It will be appreciated that different cement compositions from those described above may be prepared without departing from the concept of the present invention.

## CLAIMS

- 1 An oil well cementing composition comprising a blend of Portland cement and pozzolanic materials (blast furnace slag, fly ash, etc.) such that the chemical composition (expressed in oxides) has a  $\text{CaO/SiO}_2$  molar ratio below 1.7.
- 2 A composition as claimed in claim 1, wherein the mixture includes more than 60% of blast-furnace slag as the pozzolanic material.
- 3 A composition as claimed in claim 2, wherein the mixture comprises approximately 20% Portland cement and approximately 80% slag.
- 4 A composition as claimed in any preceding claim, wherein the mixture has a Blaine fineness of between 2,500 and 12,000  $\text{cm}^2/\text{g}$
- 5 A composition as claimed in claim 4, wherein the mixture has a Blaine fineness of between 3,000 and 5,000  $\text{cm}^2/\text{g}$ .
- 6 A composition as claimed in any preceding claim, further comprising a hollow particulate material.
- 7 A composition as claimed in claim 6, wherein the hollow particulate material comprises cenospheres, glass micro-spheres, or ceramic spheres.
- 8 A composition as claimed in any preceding claim, wherein finely divided silica is substantially absent.
- 9 A composition as claimed in any preceding claim, further comprising water and optional additives including anti-foam agents, dispersants, fluid-loss control additives, and retarders.

- 10 A composition as claimed in any preceding claim further comprising water and a dispersed gas phase so as to form a foamed cement.
- 11 The use of a composition as claimed in any preceding claim for cementing an oil, gas or water well.





Application No: GB 0208774.0  
Claims searched: 1-11

Examiner: Kathryn Orme  
Date of search: 24 September 2002

## Patents Act 1977 Search Report under Section 17

### Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:  
UK CI (Ed.T): C1H (HAV, HAW, HPP, HCH)  
Int CI (Ed.7): C04B (7/13, 7/14, 7/147, 7/153, 7/19, 7/28, 14/04, 14/22, 18/08)  
Other: Online: WPI, EPODOC, PAJ

### Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	EP 0814067 A1 (SOFITECH) see especially page 3 lines 34-36 and claims	1,6,7,8 & 9
X	EP 0618344 A2 (HALLIBURTON) see especially page 4 lines 1-7, page 6 lines 6-15 and page 7 lines 18-19	1,4,6,7,9 & 11
X	EP 0611081 A2 (HALLIBURTON) see especially page 3 lines 39-41, page 14 lines 53-56, page 17 lines 28-42 and abstract	1-4,6-9 & 11
X	US 5447198 (KUNZI ET AL) see especially claim 1 and column 6 lines 28-31	1,6-9 & 11
X	US 4933031 (BLOMBERG ET AL) see especially column 3 lines 26-36 and 45, column 4 lines 13-14	1,6,7,9 & 11
X	US 4877452 (ROUSSEL ET AL) see abstract	1-5,8 & 11
X	US 4635724 (BRUCKDORFER ET AL) see especially column 1 lines 62-63 and column 3 lines 22-23	1,6,7,9 & 11
X	WPI Abstract Accession No. 1999-125380 & JP 11001362 (Mitsubishi Materials Corp) 06/01/1999 (see abstract)	1,6,7,8 & 11

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
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